THE CATALYTIC HYDROGENATION OF PYRIDINE AT HIGH PRESSURES

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ABSTRACT

A kinetic study of the catalytic hydrogenation of pyridine and methyl substituted pyridines was made at high pressures. With these pressures ranging from 500 to 1500 p.s.i., a high pressure micro reaction vessel equipped with a shaking mechanism and heating jacket was employed. Adams' platinum oxide catalyst was used with glacial acetic acid serving as solvent for the hydrogen acceptor.

The complete hydrogenation of 0.010 mole of pyridine required slightly less than 40 minutes using 0.1000 gram of catalyst, 4.00 ml. acetic acid, an initial pressure of 1000 p.s.i., and a temperature of 30° C. The over-all reaction was found to follow first kinetics.

In the calculation of the activation energies of the pyridines, two values were obtained for each compound except the 2,3- and 2,4-dimethylpyridines for which a single value was found. The higher value, averaging 8800 calories per mole, appeared over the average temperature range of 15-34° C. The lower value of 4200 calories per mole appeared over the range of 34-70° C. This effect was not readily explainable, but possibly there was some change in adsorption of the hydrogen acceptor over different temperature ranges.

The reaction rate was directly proportional to the amount of catalyst. Equilibrium conditions were found in the range where 0.0100 to 0.1000 gram of catalyst was employed. A slight dependence of the reaction on the concentration of hydrogen acceptor was observed. The rate increased as the concentration of pyridine was decreased.

Over large pressure drops, e. g., 1000 to 500 p.s.i., the reaction was calculated to be 0.95 order. Since pressure drops of a single run were smaller than this, a first order dependence on hydrogen pressure was assumed for calculating rate constants.

The introduction of a methyl group into the pyridine ring slowed down the reaction considerably. From the study of mono- and disubstituted derivatives, the activity decreased as substitution was made alpha, beta, and gamma respectively. However, this was not the only factor affecting the rate. Assuming the nitrogen atom to be equivalent to a carbon-hydrogen unit, the more symmetrical the molecule the faster it would hydrogenate.

THE CATALYTIC HYDROGENATION OF PYRIDINE AT HIGH PRESSURES

I. INTRODUCTION

Catalytic hydrogenation is a very important reaction both in the laboratory and in industry. In the laboratory the reaction is particularly important in preparing organic compounds which are difficult to synthesize by other methods. Of chief importance is the use of the reaction to reduce aromatic ring systems which are resistant to ordinary chemical reduction.

While there is a considerable amount of information reported in the literature on different methods, conditions, and catalysts used in the reduction of most aromatic systems, no well-organized kinetic study of the reaction was reported until 1945 when H. A. Smith and workers published the first set of a series of papers on hydrogenation.[1,2,3,4] In their investigations Adams' platinum catalyst[5] was used with glacial acetic acid serving as solvent for hydrogen acceptor at an initial

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[1]Smith, H. A., Alderman, D. A., Nadig, F. W., J. Am. Chem. Soc., 67, 272 (1945).

[2]Smith, H. A., and Pennekamp, E. F. H., ibid., p. 276.

[3]Smith, H. A., and Stanfield, J. A., J. Am. Chem. Soc., 71, 81 (1949).

[4]Smith, H. A., Alderman, D. M., Shacklett, C. D., and Welch, C. M., ibid., p. 3772.

[5]Adams, R., Voorhees, V., and Shriner, R. L., Organic Synthesis, Coll. Vol. I, New York, John Wiley and Sons, Inc., 1932, p. 403.

hydrogen pressure of 64 p.s.i. The compounds studied included benzene and methyl substituted benzene derivatives, phenyl substituted aliphatic acids, methyl derivatives of benzoic acids, and cyclohexenes.

The following important conclusions were given: (1) the rate is first order with respect to pressure; (2) the reaction is zero order with respect to hydrogen acceptor; (3) the rate is directly proportional to the amount of catalyst used; and (4) the symmetrical substituion of the molecule is important in determining the reaction rate. Similar investigations have been carried out in the hydrogenation laboratories here by Trimble,[6] Hecht,[7] and Cox[8] on quinoline and methyl quinoline derivatives. At both high and low pressures similar results were obtained.

Stanfield[9] carried out an investigation of the catalytic hydrogenation of pyridine and benzoic acid, and their methyl substituted derivatives using Adams' catalyst, acetic acid, and an initial hydrogen pressure of 16 to 64 p.s.i. The above conclusions were also observed to be applicable in the case of benzoic acid and its methyl derivatives. However, the investigation of pyridine brought out two outstanding differences: (1) over large pressure drops for a single run, the rate was calculated to be 0.98 order rather than first order; and (2) increasing the concentration of hydrogen acceptor decreased the value of the rate

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[6]Trimble, A. T., "The Catalytic Hydrogenation of Quinoline," Master's Thesis, Georgia Institute of Technology, 1949.

[7]Hecht, J. L., "The Catalytic Hydrogenation of Quinolines," Master's Thesis, Georgia Institute of Technology, 1950.

[8]Cox, E. F., "The Catalytic Hydrogenation of Quinolines at High Pressures," Master's thesis, Georgia Institute of Technology, 1951.

[9]Stanfield, J. A., "The Kinetics of Catalytic Hydrogenation," Doctoral Dissertation, University of Tennessee, 1947.

constant. Another observation of interest was in the calculation of the activation energy of the reaction for which two different values were obtained in the temperature ranges 15-23° C. and 23-45° C. respectively.

Adams and Marshall's[10] techniques for low pressure hydrogenation were employed by Baker and Schuetz[11] in the high pressure hydrogenation of several aromatic compounds. Using pressures as high as 3000 p.s.i., the reductions required minutes whereas hours were necessary for the same reductions at low pressures. The kinetics were consistent with the findings of Smith and co-workers at low pressures.

The present investigation extends the work of Stanfield to studying the kinetics of the catalytic hydrogenation of pyridines at high pressure using the method employed by Baker and Schuetz. The various factors affecting the reaction rate were studied and compared with the low pressure results. There has been no similar systematic study of pyridine reported.

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[10]Adams, R., and Marshall, J. R., J. Am. Chem. Soc., 50, 1970(1928).

[11]Baker, R. H., and Schuetz, R. D., J. Am. Chem. Soc., 69, 1250 (1947).

II. THEORETICAL DISCUSSION

Chemical Kinetics

The principal aim of chemical kinetics is to predict the rates of chemical reactions and to attempt to follow the course of the reactions. Since most organic reactions are slow, some may be conveniently followed by kinetics. The study of kinetics is very important in organic chemistry since by varying concentrations, temperature, type and amounts of catalysts, it may be possible to bring about a reaction, increase the yield, possibly improve the quality of the product, or postulate the reaction mechanism.

Measurement of Reaction Rates

Rate of Reaction.--The rate of a reaction is expressed in terms of the concentration of any of the substances which are reacting or in terms of the products of the reaction.[1] Thus if a reactant has a concentration c at any time t , the rate is -dc/dt. If the rate of reaction is proportional to the unit concentration of none, one, or two of the reactants, a simple expression can represent the rate. However, a great many chemical processes are found not to occur by a simple rearrangement of atoms in a single stage. These complex reactions occur when the kinetic law is inconsistent with the stoichiometric equation for the reaction.[2] This complexity is also found in chemical reactions where

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[1]Laidler, K. J., and Glasstone, S., J. Chem. Ed., 25, 383 (1948).

[2]Laidler, K. J., Chemical Kinetics, McGraw-Hill Book Company, Inc., New York, N. Y., 1950, p. 180.

free atoms and radicals are formed as intermediates.

Order of a Reaction.--The manner in which the rate of a reaction varies with the concentration of the reactants can usually be indicated by stating the order of the reaction.

A reaction is said to be zero order when the rate is unaffected by the concentration of the reactants, the rate usually being determined by some limiting factor such as the absorption of light in a photochemical process. Thus for a reactant of concentration c at time t, the zero order rate expression is represented by:

$$-\frac{dc}{dt} = k, \tag{1}$$

where k is a constant.

In a first order reaction the rate is proportional to the concentration of one of the reactants.[3] The mathematical expression for this is:

$$-\frac{dc}{dt} = kc, \tag{2}$$

where small c is again the concentration of reactant.
Integrating equation (2) between the limits, concentration c_1 at time t_1, and c_2 at time t_2, the expression becomes:

$$-\int_{c_1}^{c_2} \frac{dc}{c} = k \int_{t_1}^{t_2} dt,$$

$$-\ln c_2 - (-\ln c_1) = k(t_2 - t_1);$$

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[3]Ibid., p. 4.

from which

$$k = \frac{2.303}{(t_2 - t_1)} \cdot \log \frac{c_1}{c_2} . \qquad (3)$$

When t_1 o, the initial concentration c , can be represented by c_o. Similarly t_2 and c_2 can be replaced so that c represents the concentration at time t . Thus equation (3) becomes:

$$\log \frac{c_o}{c} = \frac{kt}{2.303} . \qquad (4)$$

The concentration of a gas is proportional to its pressure p ; therefore equation (4) may be written:

$$\log \frac{p_o}{p} = \frac{kt}{2.303} . \qquad (5)$$

In equation (5) the fugacity of hydrogen is assumed to be proportional to the mole fraction of the hydrogen dissolved in the liquid phase. At higher pressures (1000 p.s.i.), the fugacity is not equal to the hydrogen pressure, and equation (5) is therefore slightly in error. Thus a more exact equation would be:

$$\log \frac{p_o \gamma_o}{p \gamma} = \frac{kt}{2.303} , \qquad (6)$$

where γ is the activity coefficient of the hydrogen gas. However, if the ratio $\frac{p_o}{p}$ is not large $\frac{\gamma_o}{\gamma}$ becomes unity, and equation (5) can be used to express the rate within experimental error. Equation (5) is extremely useful in catalytic hydrogenation rate studies where the reaction is first order, since readings of pressure at time intervals follow the course of the reaction. A plot of $\log \frac{p_o}{p}$ against t gives a straight line of slope

$\frac{k}{2.303}$ from which k is calculated.

A second order reaction occurs when the rate is proportional to the product of two concentrations.[4] Thus the reaction

$$A + B \rightarrow AB$$

can be expressed by:

$$-\frac{dc_A}{dt} = -\frac{dc_B}{dt} = kc_Ac_B. \qquad (7)$$

With a and b representing the initial molar concentrations of the two reactants, and x representing the number of moles of A and B reacting in time t, the rate expression is:

$$\frac{dx}{dt} = k(a-x)(b-x). \qquad (8)$$

If the initial concentrations are equal (i.e. $a = b$), equation (8) becomes:

$$\frac{dx}{dt} = k(a-x)^2 \qquad (9)$$

which upon rearrangement and integration gives:

$$\frac{1}{a-x} = kt + \text{constant}. \qquad (10)$$

At $t = 0$, $x = 0$; hence one may solve for the integration constant which when substituted into equation (10) gives:

$$k = \frac{1}{t} \cdot \frac{x}{a(a-x)} . \qquad (11)$$

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[4] Daniels, F., Outlines of Physical Chemistry, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 350.

If the reactants are not present in equivalent amounts, equation (8) can be integrated and evaluated to give the more complex expression:

$$k = \frac{2.303}{t(a-b)} \cdot \log \frac{b(a-x)}{a(b-x)}. \qquad (12)$$

Thus a reaction may be an over-all second order reaction, but it may also be first order with respect to A or B.

Most reactions do not follow the simple kinetics described here throughout the whole course of the reaction; in fact usually there are two or more different reactions taking place. Consequently, the mathematical representation of the over-all reaction is the resultant of several different rate expressions.[5] Among these complications are consecutive reactions, reverse reactions, and competing reactions.

Determination of the Order of a Reaction.--Since many reactions do not follow simple order kinetics, methods of determining the order must be devised. In general, the order of a reaction depends on the exponents of the concentration terms. Thus for the reaction $A + B + \ldots \rightarrow C$,

$$\text{Rate} = k c_A^a c_B^b \ldots\ldots , \qquad (13)$$

and the order of the reaction, n, is:

$$n = a + b + \ldots\ldots$$

Then the order of a reaction is the sum of all the exponents, and these exponents need not be whole numbers.

On the other hand, if the concentration of a reactant or a product

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[5] Ibid., p. 354.

is known at various times during a reaction, the order of the reaction can be calculated. A few of the methods will be given here.

(1) The most direct method is to substitute the data into the integrated forms of the known order equations and find if one of them gives a rate constant which does not drift as the value of t increases.

(2) The differential method[6] is based upon the fact that the instantaneous rate of a reaction of the n^{th} order involving one reactant is proportional to the n^{th} power of its concentration:

$$-\frac{dc}{dt} = kc^n. \tag{14}$$

Carrying out two experiments at different initial concentrations c_1 and c_2, it follows that:

$$-\frac{dc_1}{dt} = kc_1^n \tag{15}$$

and

$$-\frac{dc_2}{dt} = kc_2^n. \tag{16}$$

If logarithms are taken followed by subtraction and rearrangement,

$$n = \frac{\log(\frac{dc_1}{dt}) - \log(\frac{dc_2}{dt})}{\log c_1 - \log c_2}. \tag{17}$$

The order is then determined from a concentration vs. time curve by measuring slopes $(-\frac{dc}{dt})$ at two different concentrations and introducing the values into equation (17).

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[6]Laidler, K. J., op. cit. p. 3.

(3) For reactions involving pressures[7], equation (14) becomes:

$$\frac{dp}{dt} = kp^n. \tag{18}$$

Rearrangement and integration of this equation gives:

$$\frac{p^{-n+1}}{-n+1} + C = kt. \tag{19}$$

When $t = o$, the constant of integration C can be evaluated, and substitution of this value into equation (19) gives:

$$\frac{p^{-n+1} - p_o^{-n+1}}{t(-n+1)} = k. \tag{20}$$

The value of this relation will be shown later.

(4) Other methods of determining the order of a reaction are: the half life method[8], the isolation method[9], and the variation in ratio of reactants.[10]

Factors Affecting the Rate Constant

Effect of Temperature.—The rates of most chemical reactions increase as the temperature is increased. Very early it was pointed out that the logarithm of the specific rate of a reaction should be a linear function of the reciprocal of the absolute temperature.[11] This idea was extended

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[7]Stanfield, J. A., "The Kinetics of Catalytic Hydrogenation," Doctoral Dissertation, University of Tennessee, 1947, p. 99.

[8]Laidler, K. J., op. cit., p. 13.

[9]Ibid., p. 16.

[10]Daniels, F., op. cit., p. 363.

[11]Laidler, K. J., op. cit., p. 57.

by Arrhenius to a number of reactions, the relation being expressed as:

$$\log k = B - \frac{A'}{T}, \tag{21}$$

where A' and B are constants. The more common manner of expressing this is:

$$\frac{d \ln k}{dt} = \frac{E}{RT^2}, \tag{22}$$

where R is the gas constant and T the absolute temperature. E is the energy change or more frequently the activation energy. Integration of equation (22) yields:

$$\log k = \frac{-E}{2.303RT} + \text{constant}. \tag{23}$$

When log k is plotted against $\frac{1}{T}$ a straight line results, the slope of which is $\frac{-E}{2.303R}$. Hence E can be calculated.

Integration of equation (22) between limits gives:

$$\log \frac{k_2}{k_1} = \frac{E}{2.303R} \left(\frac{T_2-T_1}{T_1T_2}\right), \tag{24}$$

which is a useful equation for the correction of rate constants to some standard temperature. The Arrhenius equation applied to homogeneous, heterogeneous, and catalytic reactions.[12] This indicates that the activation energy of a catalytic reaction is a function of the catalyst as well as the reacting substances.

When a reaction is made up of two more concurrent reactions which

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[12]Hinshelwood, C. N., The Kinetics of Chemical Change in Gaseous Systems, Oxford University Press, Oxford, England, 1933, Third Ed., p. 66.

are differently influenced by temperature, two or more straight lines may result in an activation energy plot. The variation in the slope of the lines depends on the particular temperature range throughout which one reaction predominates over the other.[13] One good example of this might be found in considering the heats of adsorption of the substances in the reaction mixture. Thus at a given temperature one of the substances may be more readily adsorbed on the catalyst surface than the other. Another possibility is that the rate of desorption of product by the catalyst might be affected by temperature. At present the best explanation appears to be that there is a change in the adsorption of hydrogen acceptor on the metallic surface over different temperature ranges.

The Catalyst.--The requirements and characteristics of a good catalyst have been listed in a paper by Adkins.[14] The rate of a catalytic reaction depends upon the activity of the catalyst, this activity being determined by the number of active centers on the catalyst surface. These active centers consist of atoms whose valence forces are not entirely satisfied by other atoms in the catalytic surface.

The most important requirement of a catalyst is that it must strongly and actively adsorb the reactants, and it must also have such a small attraction for the products so that they will be desorbed. Failure of a catalyst to perform this last step of desorbing the product at the proper time results in "poisoning" of the catalyst. This phenomenon is caused by covering the catalytic surface the product or interaction between

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[13] Ibid., p. 67.

[14] Adkins, H., Ind. and Eng. Chem., 32, 1189 (1940).

molecules of product thus rendering the catalyst inactive. Foreign substances in a reaction invariably will poison the catalyst also by a similar procedure.

Hydrogen Volume.--In most reports on hydrogenation, the hydrogen void has not been considered in expressing the rate constant. It has been shown that the true rate constant varies inversely with hydrogen volume.[15] Therefore, equation (5) should be written as:

$$\log \frac{p_o}{p} = \frac{kt}{2.303v} . \qquad (24)$$

In accordance with this all rate constants reported in this work are multiplied by hydrogen volume, and the units are ml. per minute unless otherwise stated.

Effect of Solvent.--The purpose of the solvent or reaction medium is to facilitate the dispersion of the catalyst and the contact of the essential components, namely, hydrogen, catalyst, and hydrogen acceptor. The solvent, as well as other components, is probably adsorbed by the catalyst to such an extent that it may play a role in the determination of the course of the reaction.

The use of a solvent in the hydrogenation of a compound such as pyridine is especially important, since a self-poisoning effect has been observed in the reduction of pyridine[16] in the absence of a solvent. This was due to the electronic state of the nitrogen atom, the free

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[15]Fuzek, J. F., and Smith, H. A., J. Am. Chem. Soc., 70, 3743(1948).

[16]Maxted, E. B., and Walker, A. C., J. Am. Chem. Soc., 1093(1948).

electron pair leading to strong adsorption by a metallic catalyst. On the other hand if the pyridine nucleus in the form of the pyridinium ion is reduced, the nitrogen atom is in a shielded state with no poisoning observed. Acetic acid is a suitable solvent for the hydrogenation of pyridine and related compounds.

When using Adams' platinum catalyst, the best solvent is glacial acetic acid at both high[17] and low[18,19] pressures. However, pyridine hydrochloride hydrogenates more readily in absolute ethanol than in acetic acid using platinum oxide.[20]

The Mechanism

Although numerous theories have been proposed for the hydrogenation of aromatic nuclei, the exact mechanism is not definitely known. A few of these ideas will be mentioned briefly.

The most widely discussed phase of the mechanism is that of adsorption on the catalyst surface. Rideal[21] concludes that a metallic catalyst is covered with a mono-layer of chemisorbed hydrogen which is adsorbed without appreciable activation energy. The organic reactant is adsorbed above it. Thus ortho-para hydrogen conversion would occur on

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[17]Baker, R. H. and Schuetz, R. D., J. Am. Chem. Soc., 69, 1250 (1947).

[18]Adams, R., and Marshall, J. R., J. Am. Chem. Soc., 50, 1970(1928).

[19]Overhoff, J., and Wibaut, J. P., Rec. Trav. Chim., 50, 957(1931).

[20]Hamilton, T. S., and Adams, R., J. Am. Chem. Soc., 50, 2260(1928).

[21]Rideal, E. K., Chem. and Ind., 335(1943).

the metallic surface[22] due to interaction between a chemisorbed hydrogen atom and a hydrogen molecule in the dispersion or van der Waals field. While the hydrogenation of the benzene ring is first order with respect to hydrogen pressure, the rapid para-hydrogen conversion is often one half or even zero order.[23]

Eley[24] has advanced a reasonable explanation of the theory of chemisorption. This theory is derived by considering a metal to have electrons moving freely through the periodic potential field due to the positive cores of the metal. The effect of an adsorbed atom on the surface of the metal then leads to a lowering of the potential energy of the electron in the metallic surface. Thus there are two sets of localized energy levels for the electron, one on the hydrogen atom and one on the surface of the metal. If the wave functions corresponding to these energy levels overlap, we may have the formation of an electron pair bond, the second electron coming from the conduction orbital of the metal. The powerful adsorption of hydrogen on transition metals is due to the partly empty d orbitals of these metals. This gives rise to a high concentration of empty d levels in the surface which are much lower in energy than most of the s levels.

Beeck[25] and workers claimed that the slow, rate-determining,

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[22]Horrex, R. K., Greenhalgh, R. K., and Polany, M., Trans. Farraday Soc., 35, 511(1939).

[23]Ibid., p. 37.

[24]Eley, D. D., Quart. Rev. (London), 3, 209(1949).

[25]Beeck, O., Ritchie, A. W., and Wheeler, A., J. Colloid Sci., 3, 305(1948).

"activated adsorption" of hydrogen on a catalyst was not a process of adsorption. Instead they believed it was the slow sorption of hydrogen into the interior of the metal structure, that is, "hydride phase formation."

Balandin[26] has proposed the presence of two kinds of active centers: (1) k, capable of activating the adsorbed hydrogen, and (2) k' activating the hydrogen acceptor. In the case of benzene k centers are located on the metallic lattice edges with an interatomic distance of 3.52 angstrom units. The k' centers are constituted by the sextet in a plane with the interatomic distance of 2.94 angstroms.

The variation in the relative activity of many organic compounds with varying size and shape of the molecules indicates that steric factors may determine the rate, nature, and amount of product produced. Linstead[27] and Smith[28] have investigated this possibility. Although these workers disagreed as to the mechanism of catalyst surface adsorption of aromatic ring systems, they found two main types of steric hindrance (1) between the catalyst surface and adsorbed molecules, and (2) the adsorbed molecule blocking the approaching hydrogen from the catalyst surface.

Pullman[29] brought out an interesting concept as to the mechanism which follows the adsorption of hydrogen and acceptor. His theory was

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[26]Balandin, A. A., Bull. Acad. Sci. U.R.S.S., Clase Sci. Chim., 339(1945).

[27]Linstead, R. P., Doering, W. E., Davis, S. B., Levine, P., and Whetstone, R. R., J. Am. Chem. Soc., 64, 1985(1942).

[28]Smith, H. A., Alderman, D. M., and Nadig, F. W., J. Am. Chem. Soc., 67, 272(1945).

[29]Pullman, A. and Daudel, R., Compt. Rend. 221, 298(1945).

based on the fact that molecules generally add upon the most highly charged bonds (where π electron charge is greatest) or on a combination of two charged positions to which free atoms can add. Thus benzene has six bonds of low charge, and the reaction starts slowly. However, once the reaction begins, the ring is reduced immediately to cyclohexane without stopping at intermediates. To explain this the first hydrogen molecule adds to one of the six bonds, giving the dihydro compound. The dihydro compound now has two more highly charged bonds than does benzene, and it therefore immediately adds two more hydrogen molecules. This concept seems to explain why no partly hydrogenated intermediate has been isolated in the hydrogenation of the benzene ring.

Recently excellent reviews of the mechanism of surface reactions involving hydrogen[30] and adsorption on metallic surfaces[31,32] have been published.

To conclude this section it may be said that the following steps take place in the hydrogenation of an aromatic ring: (1) hydrogen is adsorbed on the metallic surface with a very small activation energy;[33,34] (2) the organic reactant is adsorbed; (3) steric factors determine the rate with which a hydrogen molecule adds across the double bond; (4) the reaction proceeds so fast through the formation of intermediates, that it is not possible to isolate them; and (5) the products are desorbed.

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[30]Laidler, K. J., J. Phys. and Colloid Chem., 55, 1067(1951).

[31]Farkas, A., Ibid., 1013.

[32]Eley, D. D., Ibid., 1017.

[33]Taylor, H. S., J. Am. Chem. Soc., 53, 578(1931).

[34]Beeck, O., Phys. Rev., 47, 61(1945).

III. EXPERIMENTAL

Materials

Pyridines.--High purity pyridine was obtained from the J. T. Baker Chemical Company, Phillipsburg, New Jersey. The greatest impurity reported was 0.7% water content. The sample was placed in a brown bottle and dried over sodium hydroxide pellets for two weeks. Further purification of pyridine was made by distillation through a packed column under nitrogen, and the fractions were stored in brown bottles under an atmosphere of nitrogen. The five foot column had a diameter of 19 mm. with a distillation head of the total-reflux, partial take-off type. The column was packed with single-turn glass helices and had an efficiency of about 40 theoretical plates.

The samples of 2-methyl-, 2,4-dimethyl-, and 2,6-dimethyl-, and 2,4,6-trimethylpyridines were gifts from the Koppers Company, Inc., Pittsburgh, Pennsylvania. The Matheson Company, Inc., East Rutherford, New Jersey furnished 2,3-dimethyl-, 2,4-dimethyl-, and 2,4,6-trimethylpyridines. A sample of 2,5-dimethylpyridine was purchased from the Reilly Tar and Chemical Corporation, Indianapolis, Indiana. All of these samples were also purified by distillation under nitrogen after storage in contact with sodium hydroxide pellets.

The reflux ratio used in all of these distillations was usually eight to one. Total immersion thermometers were used for taking the head temperature, and the boiling points listed in Table 1 are corrected for exposed stem as well as barometric pressure. It was deemed necessary

Table 1. Boiling Points.

Compound	Boiling Point, °C. (corrected)	Boiling Point, °C. (literature)[1]
Pyridine	115.3	115.5
2-methylpyridine	129.4	129.0
4-methylpyridine	144.2	143.1
2,3-dimethylpyridine	161.6	163.0
2,4-dimethylpyridine	159.2	157.9
2,5-dimethylpyridine	156.4	156.5
2,6-dimethylpyridine	143.9	142.3
2,4,6-trimethylpyridine	171.2	171.2

[1]Heilbron, I. M., Dictionary of Organic Compounds, New York, Oxford University Press, 1943.

to keep the pyridines under nitrogen whenever possible as they are easily oxidized and absorb water when exposed to the atmosphere. This, of course, might possibly lead to poisoning of the catalyst or to small amounts of side reactions. A striking characteristic of pyridine and its homologs is the foul odor of their vapors when a very small amount of impurity is present. On the other hand, freshly distilled material does not have too noticeable an odor.

Catalyst.--A platinum oxide catalyst, prepared by the American Platinum Works, Newark, New Jersey, was used throughout this work. The catalyst sample was marked "Catalyst II" and contained 81.16 per cent platinum.

Acetic Acid.--Glacial acetic acid was purified by distillation through the five foot helix packed column. The corrected boiling point of the acid was 118.1° C. which corresponded to the normal boiling point.[2]

Hydrogen.--The National Cylinder Gas Company, Atlanta, Georgia, supplied the hydrogen gas. When preparing for a run, the gas was allowed to pass directly into the hydrogenation bomb without any purification. Pressures from 500 to 1500 p.s.i. were used.

Apparatus

The high-pressure reaction vessel was the Aminco[3] micro apparatus equipped with heater and shaking mechanism, valve, and gage. The required construction and operation of the superpressure equipment for

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[2]Weissberger, A., and Proskauer, E., Organic Solvents, Oxford University Press, 1935, p. 43.

[3]American Instrument Company, Silver Spring, Maryland.

hydrogenation has been discussed by Adkins.[4]

Shaker.--The shaking mechanism consisted of a heavy cast iron base on which was mounted a pedestal for supporting an oscillating trunnion. The heating jacket was attached to the trunnion, and the removable reaction bomb could be placed in position inside the heater. A motor was used to rock the vessel in an arc of about 30 degrees at 34 cycles per minute.

Reaction Vessel.--The reaction bomb was made of manganese steel with an outside diameter of 2.57 inches and an outside length of 11.75 inches. The volume of the bomb was 43 ml. An inner pressure head with a copper gasket fitted on the bomb; the inner head was connected to the needle valve, and the needle valve in turn attached to the dial pressure gage. A hardened steel ring was seated on the inner head, and finally an outside compression cap was screwed on the bomb. In high pressure work it is important that the amount of thrust bolt pressure applied on the periphery of the closure is uniform. For this purpose a flash signal torque wrench was obtained. The assembled pressure mechanism was built to withstand 26,000 p.s.i.

Temperature Control.--The heating jacket had two interwoven elements wound in parallel and controlled with a three-heat switch. With the switch in the "Low" position, both heater elements were in series to give quarter wattage. The heater was connected to a Powerstat voltage regulator, which in turn was connected to a constant voltage box. Thus the

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[4]Adkins, H., J. Am. Chem. Soc., 55, 4272(1933).

temperature could be controlled accurately by varying the voltage supplied by the Powerstat. The temperature was read from a Weston testing thermometer placed through the end of the heating jacket and into the thermowell of the vessel.

Reaction Liners.--It was necessary to use glass liners to prevent contamination of the reaction mixture and corrosion of the bomb. All liners used were made in this laboratory from pyrex test tubes.[5] The liners were fitted with ground glass tops and had a small hole in the side to admit hydrogen into the reaction mixture. The volume of the bomb including the gage, valve, and each liner ranged from 45 to 47 ml. From this the volume available to hydrogen for each run could be determined. This was shown previously to be an important factor in evaluating the rate constant.

Procedure

Familiarization of Equipment.--In order to learn the hydrogenation technique, several practice runs were made using benzoic acid as the hydrogen acceptor, glacial acetic acid solvent, and the platinum oxide catalyst. In these runs, such difficulties as leakages were overcome and reading of the gage and general techniques were perfected.

Measurements.--Each catalyst sample was weighed on an analytical balance on tared watch glasses and transferred to the pyrex liner with a camel's hair brush.

The glacial acetic acid was always measured with a clean, dry 4 ml.

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[5]Cox, E. F., "The Catalytic Hydrogenation of Quinolines at High Pressures," Master's Thesis, Georgia Institute of Technology, 1951, p. 18.

pipette.

A sampling device similar to the one employed by Hecht[6] was designed for an accurate delivery of the desired weight of a particular pyridine sample under nitrogen. Either 6 mm. glass tubing or inverted 1.00 ml. pipettes were calibrated and used for this purpose. This method gave a fairly rapid measurement, and of more importance, prevented the sample from coming into contact with the air. The accuracy of this method varied between 0.5 per cent and 1.0 per cent.

Standard Conditions.--A set of "standard conditions" were prescribed, and comparison of reaction rates for the pyridines were made under this set of conditions. These standard conditions were the following: 0.010 mole of hydrogen acceptor; 0.1000 gram catalyst; a temperature of 30° C.; an initial hydrogen pressure (gage) of 1000 p.s.i.; and finally, 4.00 ml. of glacial acetic acid. Thus kinetic studies could be made by varying one of the conditions and holding all others constant. The variations made are shown in Table 2.

Experimental Technique.--Of prime importance was the problem of having the apparatus reach the desired constant temperature. Whenever possible the assembled bomb, minus reaction mixture, was placed in the shaking mechanism several hours before a run was to be made. The bomb was removed for charging and then placed back in the shaker and allowed to stand for about thirty minutes before the reaction was started. Calibrations for desired temperatures were made by varying the input voltage and observing

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[6]Hecht, J. L., "The Catalytic Hydrogenation of Quinolines," Master's Thesis, Georgia Institute of Technology, 1950, p. 28.

Table 2. Rate Study Conditions.

Variable	Amount Varied
Hydrogen Acceptor	0.010, 0.020, 0.040 mole
Catalyst	0.0100, 0.0250, 0.0500, 0.1000, 0.1500, 0.200 g.
Initial Pressure	500, 1000, 1500 p.s.i.
Temperature	15° to 70° C.
Solvent	4.00 ml. and 8.00 ml.

the corresponding constant temperature. With such a small amount of reacting materials in the bomb, there were no rises in temperature noted due to the heat of hydrogenation. Thus during a run retaining of a constant temperature was not a problem.

The first step in charging the bomb was to transfer the accurately weighed catalyst to the glass liner. While flushing dry nitrogen through the sampling apparatus, the acetic acid was added to the liner. After adding the pyridine sample and placing the ground glass top in the liner, the reaction mixture was carefully placed in the bomb with the vent hole in a known position. The bomb was always assembled so that the vent hole would be up at all times. Placing the bomb in a special vise the head was assembled, using considerable care in tightening the thrust bolts with the torque wrench. With the head and gage in place, hydrogen was passed in directly from the tank to the desired pressure. The charged and assembled bomb was then placed in the heating jacket and locked in securely. When constant temperature was attained, the rocking was started, and pressure readings were recorded at desired time intervals.

Cleanliness was of upmost importance in all the operations involved in the above procedure. Special attention was given to the liners and the sampling apparatus. The liners were allowed to stand in cleaning solution overnight after which they were rinsed several times with both tap and distilled water. Thorough drying in an oven at 110° C. was next effected. The calibrated tube was rinsed with acetone and dried in a stream of nitrogen. The inside of the bomb was rinsed with methanol and swabbed with a clean towel after each run.

Isolation of Hydrogenated Products.--

The products of the hydrogenation of pyridines in this work are well known to be the corresponding piperidines. The reported yield of piperidine is usually high, many times approaching a quantitative yield. However, under more drastic conditions,[7] different catalysts, or different solvents,[8] other products might result due to cleavage of carbon to nitrogen bonds and loss of ammonia or formation of condensation compounds.

It did not seem necessary to carry out an extensive investigation as to the identification of the products. However, several distillations were carried out to compare the approximate yield of the piperidines under the conditions used with yields obtained under other hydrogenation conditions.

The first step in isolating the product was to filter off the spent catalyst by means of a sintered glass funnel. The excess acetic acid was removed by distillation, leaving a residue which was the piperidinium acetate salt. The salt was cooled and added to an excess of 20 per cent sodium hydroxide solution. If an organic layer appeared, it was separated from the basic layer. The basic layer was carefully extracted several times with ether, the ether layer being added to the previously mentioned organic layer. After this mixture was dried over sodium hydroxide pellets, the ether was removed by distillation, and a fractional distillation was carried out on the remaining piperidine. A small, 7 mm., 12-inch Vigreau column with a total-reflux, partial

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[7]Sebatier, P., and Mailke, A., Compt. Rend., 144, 784(1907).

[8]Arens, J. F., and Wibaut, J. P., Rec. Trav. Chim., 61, 452(1942).

take-off head was used for the distillation. The process was carried out under nitrogen to prevent the possible oxidation of the material.

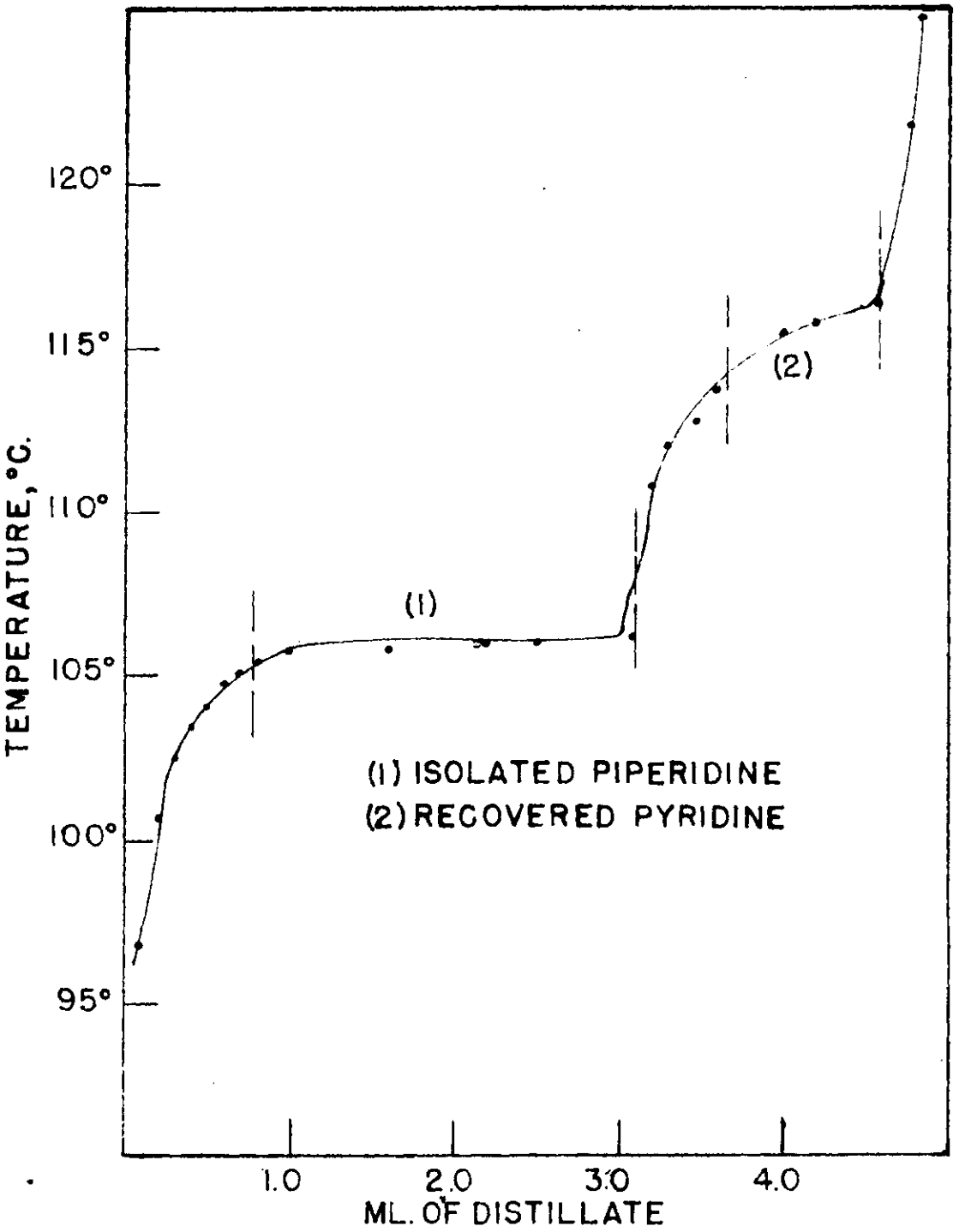
The distillations were carried out on the hydrogenation products from four or five runs. The results of three of these are shown in Table 3, and the recovery of hydrogenated product is shown to approach ninety per cent. Distillation I shows that the yield of product from a pyridine hydrogenation taken to completion (88 per cent yield), while Distillation II is an example of the complete reduction of 2-methyl-pyridine (86 per cent). By complete hydrogenation we mean that the reaction was carried out until no further pressure drop could be detected. Also this constant pressure value was near the calculated absorption of three equivalent moles of hydrogen. Distillation III was of particular interest since it was of reaction mixtures which were stopped when they had proceeded to two-thirds completion. The purpose of this, of course was to determine if any intermediate hydropyridines could be isolated. No intermediates were indicated from the fractionation. Instead 32 per cent of the pyridine was recovered, and 53 per cent piperidine was fractionated. A plot of volume vs. temperature for the last distillation is shown in Graph I, and the significance of this particular distillation will be taken up in more detail in the next section.

Table 3. Isolation of Products.

	Distillation		
	I	II*	III
Moles Pyridine	0.04	0.04	0.04
Moles Pyridine (I) recovered	-	-	0.0161
Observed B. P., °C.(I)	-	-	115.2-116.0
Moles Piperidine (II) recovered	0.0352	0.0340	0.0262
Observed B.P., °C.(II)	105.0-105.4	117.8-118.4	105.4-106.0
Per cent pyridine recovery	-	-	32%
Per cent piperidine recovery	88%	86%	52%

*Distillation II was 2-methylpiperidine.

GRAPH I.



DISTILLATION CURVE FOR TWO-THIRDS HYDROGENATED PYRIDINE

IV. DISCUSSION OF RESULTS

Previous Literature

The first reported reduction of pyridine to piperidine was performed by Skita and Meyer[1] using colloidal platinum in acetic acid at low pressure. Previously Sebatier[2] had failed to produce any piperidine by passing pyridine vapors and hydrogen over a heated nickel catalyst. Skita and Bruner[3] hydrogenated 3 grams of pyridine with 0.26 gram of colloidal platinum at low pressure in 50 minutes. Larger amounts of pyridine were reduced under the same conditions but required a longer period of time. Under similar conditions 2-methylpyridine (3.5 hours), 2,4-dimethylpyridine (9 hours), and 2,4,6-trimethylpyridine were reduced. Zelinskii[4] readily reduced pyridine in an open tube with either platinized or palladinized asbestos.

In the early hydrogenation methods of reducing aromatic nuclei, colloidal platinum and palladium[5] were used widely. However, these catalysts were limited to use in comparatively few solvents, and there was frequent difficulty in isolating the products. Voorhees and Adams[6] introduced platinum black as a more active and efficient catalyst since

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[1]Skita, A., and Meyer, W. A., Ber., 45, 3589(1912).

[2]Sebatier, P., and Mailke, A., Compt. Rend., 144, 784(1907).

[3]Skita, A., and Bruner, W., Ber., 49, 1597(1916).

[4]Zelinskii, N. D., and Borisov, P., Ber., 57B, 150(1924).

[5]Willstatter, R., and Hatt, D., Ber., 45, 1471(1912).

[6]Voorhees, V., and Adams, R., J. Am. Chem. Soc., 44, 1397(1922).

it could be used in most solvents and could easily be filtered from the reaction products. The relative effect of platinum, palladium, iridium, and osmium was studied, and the activity was found to decrease in that order.[7] Raney nickel and nickel on keiselguhr catalysts were employed by Adkins and others.[8,9] Here the control of temperature was an important factor because of side reactions such as cleavage of the carbon to nitrogen bond, alkylation of the amine formed, or condensation of intermediates. Good yields have been reported from hydrogenations in which the nickel on silica gel catalyst were used.[10,11] All of the above mentioned hydrogenations were carried out on pyridine at low pressures.

Ipatiev[12] introduced high pressure hydrogenation in 1904, but the method was not widely used until the improvements in the alloys for the bombs and design of reaction equipment made high pressure reductions less expensive, more convenient, and safer. One of the first high pressure hydrogenations of the pyridine ring was carried out by Sadikov.[13] The conditions were quite drastic - 152 atmospheres hydrogen pressure and

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[7]Sadikov, V. S., and Mikhailov, A. K., J. Chem. Soc., 438(1928).

[8]Adkins, H., Kuick, L. F., Farlow, M., and Wojick, B., J. Am. Chem. Soc., 56, 2425(1934).

[9]Covert, L. W., and Adkins, H., J. Am. Chem. Soc., 54, 4116(1932).

[10]Ushakov, M. I., Bronevskii, A. I., and Ivanova, M. I., Org. Chem. Ind. (U.S.S.R.), 5, 33(1938).

[11]Ushakov, M. I., Livshitz, S. S., Zhdanova, N. V., Bull. Soc. Chim., (5), 2, 573(1935).

[12]Ipatieff, V. N., Catalytic Reactions at High Pressures and Temperatures, The Macmillan Company, New York, New York, 1937.

[13]Sadikov, V. S., and Mikhailov, A. K., op. cit, p. 440.

250° C. The yield of piperidine was only 20 per cent, and only 30 per cent pyridine recovery was reported. It is very likely that the conditions employed caused considerable decomposition. A theoretical conversion of pyridine to piperidine was carried out over a nickel-silica gel catalyst at 150° C. and 50-100 atmospheres pressure.[14] The time required was five hours, and 2-methylpyridine was similarly reduced in seven hours. Using either a copper or nickel catalyst, Sugimo[15] reported a quantitative conversion at 220-30° C. and 160 atmospheres of hydrogen. There have been no high pressure hydrogenations of pyridine under conditions used in this thesis reported in the literature.

As mentioned previously, a very extensive study of the kinetics of pyridine hydrogenation was made by Stanfield,[16] using platinum oxide, acetic acid solvent, and low pressures. In the following sections his results are compared with the results from the hydrogenations of this investigation. Some of the important results from his and other workers might be briefly mentioned.

The rate of hydrogenation of pyridines decreased with the introduction of a methyl group into the ring.[17] It was also found that the greater the distance between the methyl group and the nuclear nitrogen atom, the slower the rate became. A third noticeable effect was one of

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[14]Ushakov, M. I., and Bronevskii, A. I., J. Gen. Chem. (U.S.S.R), 7, 750(1937).

[15]Sugimo, K., and Mizuguichi, J., J. Chem. Soc. Japan, 59, 867(1938).

[16]Stanfield, J. A., "The Kinetics of Catalytic Hydrogenation, Doctoral Dissertation, University of Tennessee, 1947.

[17]Ushakov, M. I., and Bronevskii, A. I., op. cit., p. 793.

symmetry,[18] that is, considering the nitrogen atom in the pyridine ring equivalent to a carbon atom in the benzene ring. Thus symmetrical methyl substitution led to a more readily reducible compound. In addition to the above results, Stanfield[19] came to the following conclusions in his kinetic studies:

(1) The reaction was directly proportional to the amount of catalyst used;

(2) Increasing the pyridine concentration decreased the rate constant;

(3) The rate was not exactly first order with respect to hydrogen pressure over large pressure drops but was calculated to be 0.98 order. However, for pressure ranges of a single run, the first order equation could be applied.

(4) Two values for the activation energy were found, one averaging 10,500 calories per mole (15-23° C.) and the other 4500 calories per mole (23-45° C.).

The Rate Curve

Calculation.--In a previous section the equation

$$\log \frac{p_o}{p} = \frac{kt}{2.303} \qquad (1)$$

was derived for a first order reaction. When $\log \frac{p_o}{p}$ is plotted against time t, a straight line of slope $\frac{k}{2.303}$ should result, and the rate constant k can be calculated. Inasmuch as it has been shown previously,

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[18] Stanfield, J. A., op. cit., p. 94.

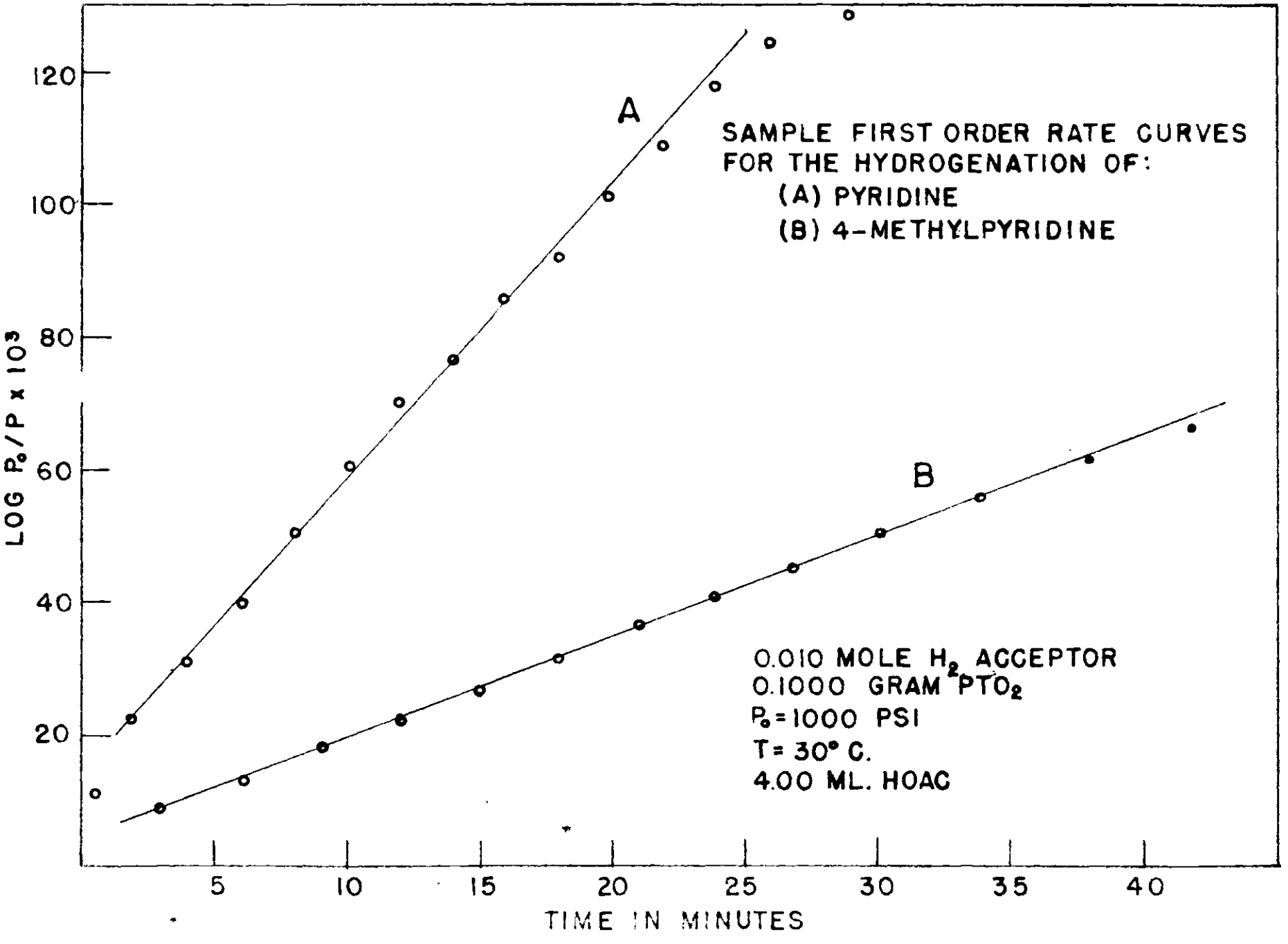
[19] Ibid., pp. 74,90, and 99.

to obtain the true constant, this value must be multiplied by the volume, and all rates reported here are Kv values.

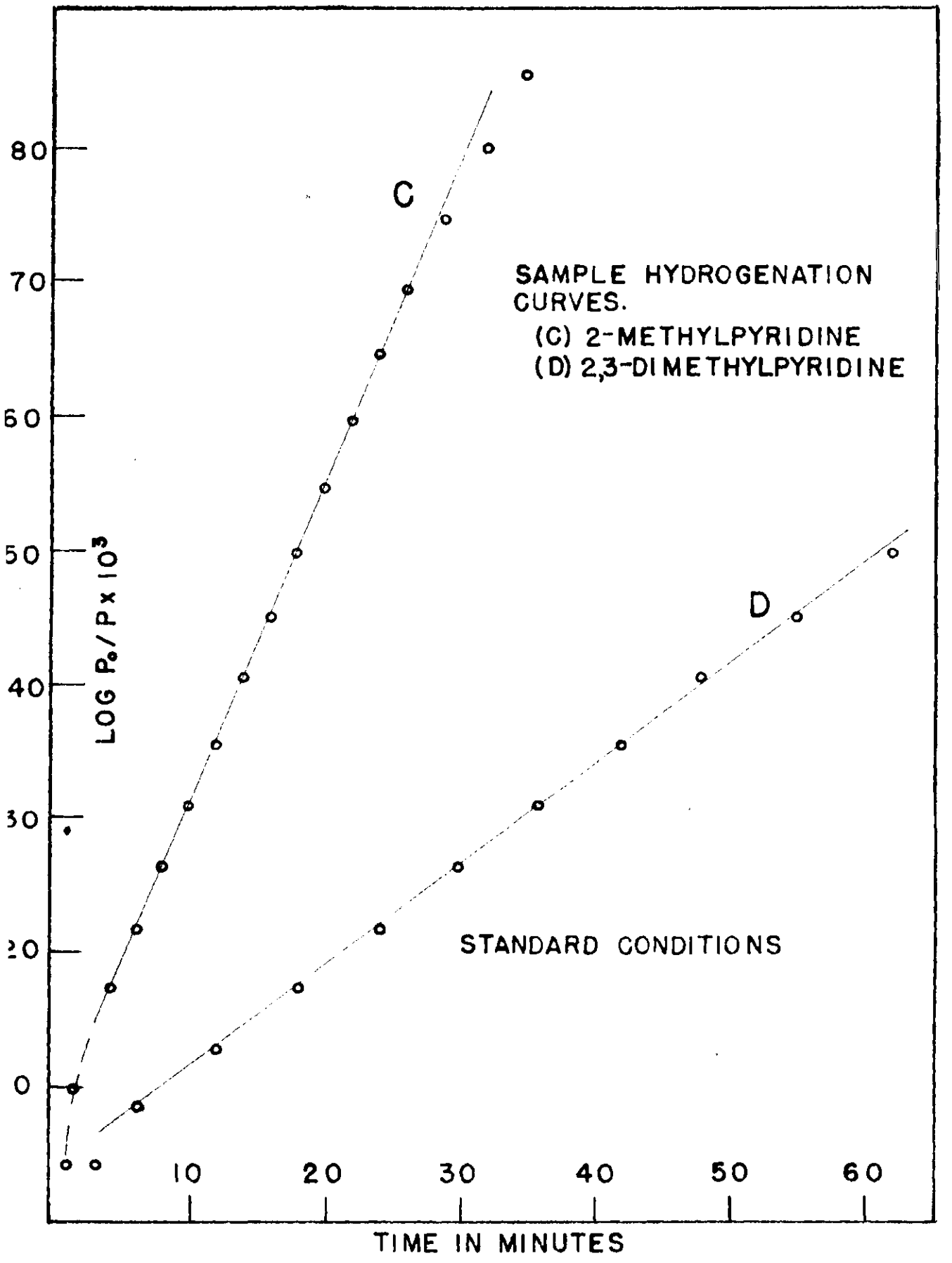
A noticeable drifting off in the rate curve was observed in some of the runs, and even in some of these, "breaks" appeared in the curve. The term "break" will be used to mean a discontinuity in the slope. These "breaks" were most important in runs which were particularly slow and also when the concentration of pyridine was increased. Explanations for these findings will be given during the course of the chapter. However, it was important to investigate the possibility of the reaction not following simple first order kinetics with respect to hydrogen pressure. Calculations which are also discussed later, showed the reaction to be 0.95 order. This value was for large differences in pressure, namely 500 to 1000 p.s.i. and 1000-1500 p.s.i. Since the pressure drop for each run was only between 100 and 300 p.s.i., rate constants have been calculated as above, thus assuming first order dependence on hydrogen pressure. The first portion of each curve was used for calculating Kv values.

Nature of the Curve.--In Graphs II and III typical examples are given for the hydrogenation of pyridines. Plot A is of pyridine itself and plot B of 4-methylpyridine, both under standard conditions. These two plots show that the first order rate law was obeyed. The slight drifting of the curve near the end of the run may be attributed to poisoning of the catalyst. A good example of the runs which had "breaks" in the curve can be seen in Graph VI. This was a hydrogenation of 0.02 mole pyridine. Possibly in a longer run such as this, the poisoning effect is more apt to show up in the curve. It was necessary to take considerable care in

GRAPH II.


120
100
80
60
40
20
LOG $P_o/P \times 10^3$
A
B
SAMPLE FIRST ORDER RATE CURVES
FOR THE HYDROGENATION OF:
(A) PYRIDINE
(B) 4-METHYLPYRIDINE
0.010 MOLE H_2 ACCEPTOR
0.1000 GRAM PTO_2
P_o = 1000 PSI
T = 30° C.
4.00 ML. HOAC
5
10
15
20
25
30
35
40
TIME IN MINUTES

GRAPH III


80
70
60
50
40
30
20
0
LOG $P_o/P \times 10^3$
C
D
SAMPLE HYDROGENATION CURVES.
(C) 2-METHYLPYRIDINE
(D) 2,3-DIMETHYLPYRIDINE
STANDARD CONDITIONS
10
20
30
40
50
60
TIME IN MINUTES

selecting time intervals for reading the gage so that accurate pressure readings could be made. Plot D represents the hydrogenation of 2,3-dimethylpyridine under standard conditions. Plot C gave a good illustration of the rapid initial drop in hydrogen pressure which was observed in most of the runs. This is a good indication as to the initial step in the reaction - that of the adsorption of hydrogen on the catalyst surface. This rapid decrease in pressure was not observed until the shaking was begun.

Activation Energies

The activation energy for a reaction is easily calculated from a plot of log K versus $\frac{1}{T}$. The straight line obtained was a slope which equals $\frac{-E}{2.303R}$. In evaluating the E values for methylpyridines, Stanfield[20] obtained two straight lines. This means that some effect is operating in one temperature range and not in the other, possibly some change in adsorption or catalytic activity.[21] These runs were made over temperature ranges from 15° C. to 45° C., the breaking point occurring in the 22-25° C. range. The higher activation energy which was in the lower temperature range was 10,500 calories per mole (average value), and the value in the higher temperature range was 4500 calories per mole.

Similar results were obtained in the present high temperature kinetic study. However, plots of the temperature run of 2,3- and 2,4-dimethylpyridines showed no indication of a break in the activation energy curve. The E values of the other pyridines showed the breaks, but they were in general at a higher temperature than where they appeared in

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[20] Ibid, pp. 84 and 94.

[21] See previous discussion of this in Chapter II.

the low pressure work. Sample plots of the two types of values found for the activation energy are shown in Graphs IV and V. Enough runs were made to give at least three points on either side of the breaking point of the two lines. Table 4 lists the E values for all of the pyridines studied. The break point ranged from 27° with pyridine to 42° with 4-methylpyridine. The average activation energy value for the low temperature range was 4200 calories per mole; that for the higher temperature range was 8800 calories per mole.

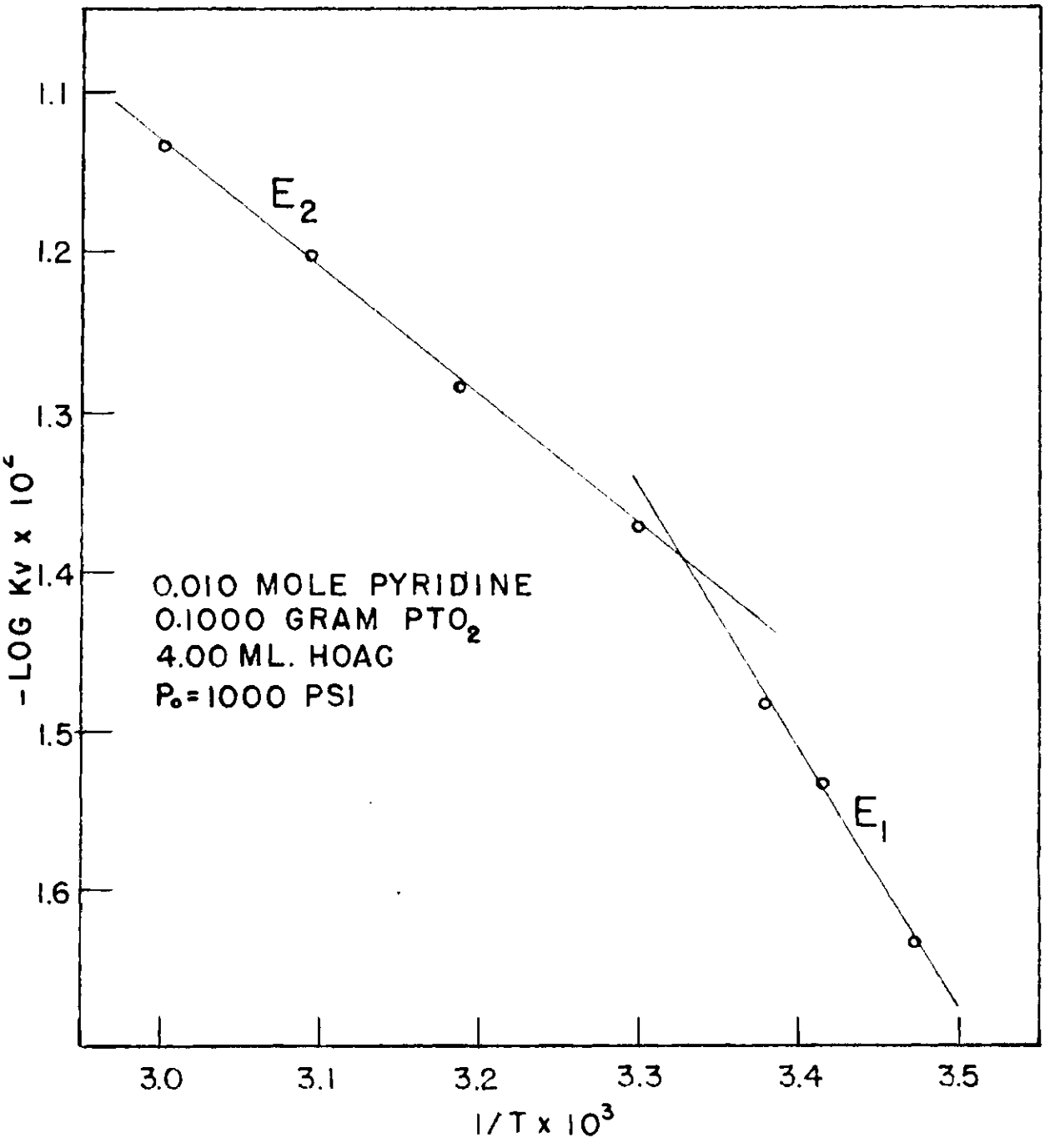
All conditions were the same in Table 4, that is 0.010 mole hydrogen acceptor, 0.1000 gram catalyst, p_o = 1000 p.s.i., and 4.00 ml. acetic acid solvent.

The Effect of Methyl Substitution

The effect of structure on the reaction rate is shown in Table 5. The introduction of a methyl group slows down considerably the rate of hydrogenation of the pyridine ring. Apparently in the mono-methylpyridines the activity decreases as a methyl group is substituted alpha, beta, and gamma, respectively. This is also shown to be the case when the activities of the disubstituted derivatives are compared. Thus the rate decreases as the distance between the introduced methyl group and ring nitrogen increases.

The 2,6 derivative reduced the fastest of the disubstituted pyridines as would be expected from the above conclusions. It is interesting to note that both the 2,5 and 2,6 isomers hydrogenated more readily than did 4-methylpyridine which is a further indication that the activity is alpha > beta > gamma. However, the fact that the methyl groups in the 2,5 compound are para to one another indicates that symmetry contributes

GRAPH IV

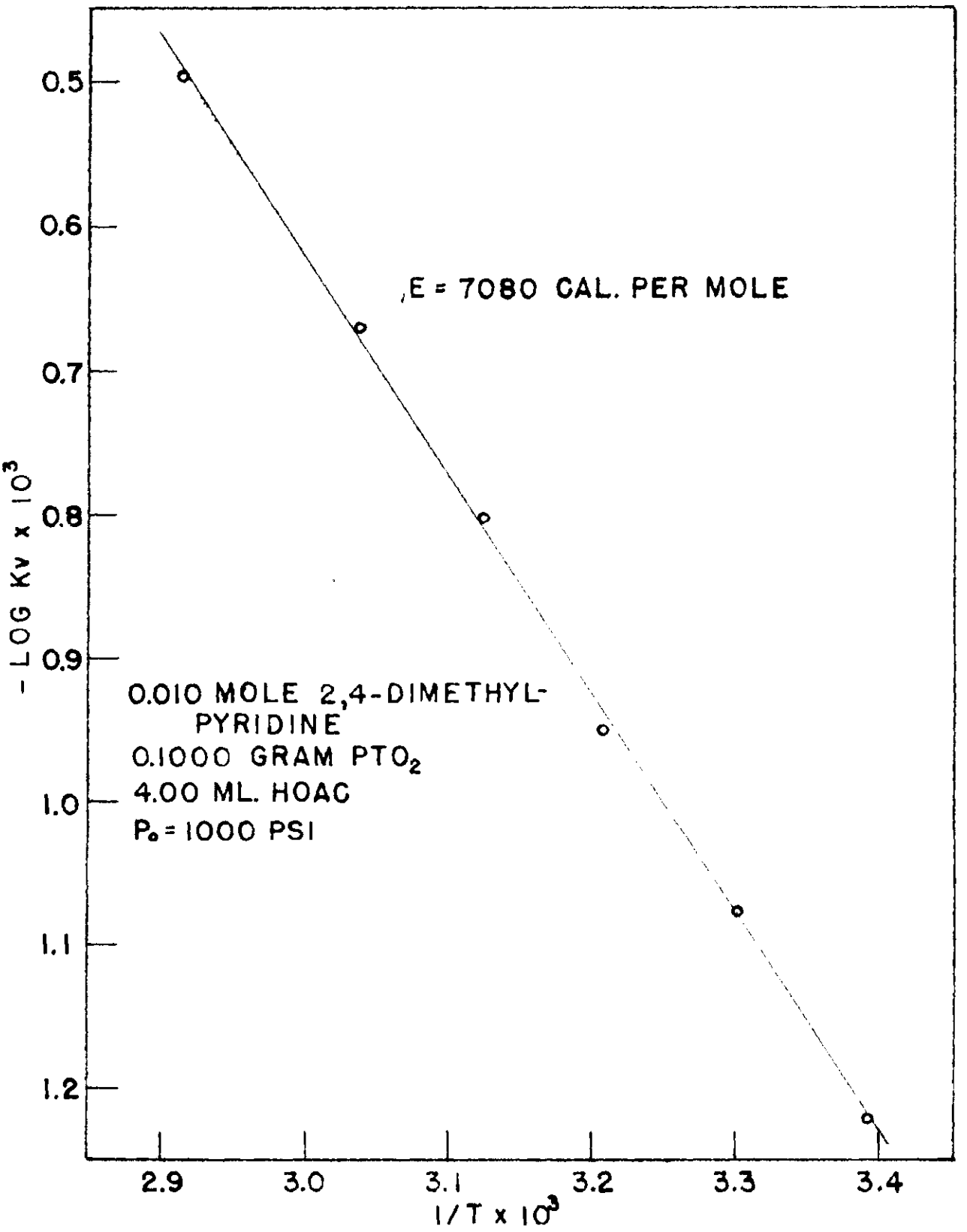


ACTIVATION ENERGY OF PYRIDINE

E_1 = 7410 CAL. PER MOLE

E_2 = 3710 CAL. PER MOLE

GRAPH V



ACTIVATION ENERGY OF 2,4-DIMETHYL-PYRIDINE

Table 4. Activation Energies.

Compound	E_1 (Lower temp. range)	E_2 (Higher temp. range)	Break in Curve at °C.(appr.)
Pyridine	8410	3710	27°
2-methylpyridine	8320	3800	39°
4-methylpyridine	6640	3940	42°
2,3-dimethylpyridine	8480	-	-
2,4-dimethylpyridine	7080	-	-
2,5-dimethylpyridine	11100	4210	37°
2,6-dimethylpyridine	13900	5210	30°
2,4,6-trimethylpyridine	7450	4170	32°
Average	8800	4200*	34°

*Does not include 2,3- and 2,4-dimethyl values.

Table 5. Effect of Structure.

Part A. 0.010 Mole Acceptor

Compound	Kv x 10^3	Relative Rate
Pyridine	423	100
2-methylpyridine	276	65
2,6-dimethylpyridine	178	42
2,5-dimethylpyridine	145	34
4-methylpyridine	137	32
2,4-dimethylpyridine	84.5	20
2,3-dimethylpyridine	64.7	16
2,4,6-trimethylpyridine	52.3	12

All values are for standard conditions.

Part B. 0.020 and 0.040 Moles Acceptor

Pyridine Derivative	Moles Acceptor	Kv x 10^3	Relative Rate
Pyridine	0.02	367	100
	0.04	343	100
2-methyl-	0.02	256	69
	0.04	246	72
2,6-dimethyl-	0.02	146	40
	0.04	141	41

to the activity of the molecule. This is shown to be the case when the rates of the 2,5 and 2,3 isomers are compared, the rate of 2,5 being twice that of 2,3. For this concept of symmetry, one must assume that the ring nitrogen atom be considered as equivalent to a carbon-hydrogen unit. Since alpha and beta substitutions render the pyridine nucleus more active towards hydrogenation than does gamma substitution, the 2,3 disubstituted derivative would be expected to reduce more readily than the isomeric 2,4 compound. However, the 2,4-dimethylpyridine has a faster rate constant than the 2,3 isomer. In this case, evidently the symmetry effect was more important than was the distance between the nitrogen atom and the methyl groups.

The only trimethyl substituted derivative studied was 2,4,6-collidine, and it was found to have the slowest rate constant of all the pyridines listed in Table 5. Since it is a symmetrical molecule it would be expected to be more susceptible to hydrogenation than other trimethyl isomers.

The conclusions made above are similar to those made in the low pressure work of Stanfield.[22] Table 6 compares the relative hydrogenation rates of the various pyridines at high and low pressures, other conditions being the same. Since the symmetry factor definitely influences the reaction rate, it was of interest to compare relative rates with the low pressure runs on corresponding methylbenzenes.[23]

In comparing the low and high pressure data, the most striking thing is that methyl substitution does not decrease the rate as much at

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[22] Ibid., p. 94.

[23] Smith, H. A., and Pennekamp, E. F. H., J. Am. Chem. Soc., 67, 276(1945).

Table 6. Comparison of Relative Hydrogenation Rates.

Pyridine Derivative	Relative Rate 32 p.s.i.	Relative Rate 1000 p.s.i.	Corresponding Benzene
Pyridine	100	100	Benzene(100)
2-methyl-	36	65	toluene(62)
2,6-dimethyl-	25	42	meta xylene(49)
2,5-dimethyl-	25	34	para xylene(65)
4-methyl-	20	32	-
2,4-dimethyl-	13	20	-
2,3-dimethyl-	11	16	ortho xylene(32)
2,4,6-trimethyl-	11	12	mesitylene(58)

high pressure. Otherwise the results are quite similar except for the values of 2,4,6-collidine. At 16 and 64 p.s.i. this compound hydrogenated faster than both 2,4- and 2,3-dimethylpyridines. Also at 64 p.s.i. the rate for 2,3-dimethylpyridine was greater than that for the 2,4 isomer. In the third column the symmetry effect shows up very well in the benzene series. The relative rate value of mesitylene is of special interest. However, a comparison of this with 2,4,6-collidine shows that symmetrical substitution is definitely not the only factor in play in the pyridine series.

Effect of Concentration of Hydrogen Acceptor

In the high pressure hydrogenation reported by Baker[24] There was a zero order dependence on the hydrogen acceptor, but pyridine was not among the compounds studied. The present research showed that there was a slight dependence of the concentration of pyridine on the rate constant. This dependence has also been observed in low pressure work.[25] This is not readily explainable. One plausible explanation can be found in considering the amount of solvent used. In the 43 ml. bomb the volume of solvent had to be kept low because of the safety factor of having less than half of the bomb occupied by liquid. Thus the standard 4.00 ml. volume of acetic acid led to a high pyridine concentration; for example, a run using 0.04 mole hydrogen acceptor contained almost equal volumes of the two liquids. This led to a very high pyridine concentration for the amount of catalyst used, facilitating the poisoning of the catalyst surface.

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[24]Baker, R. H., and Schuetz, R. D., J. Am. Chem. Soc., 69, 1250(1947).

[25]Stanfield, J. A., op. cit., p. 90.

As a test for the above explanation, several runs were made doubling the volume of solvent. This decreased the pyridine concentration, and a faster rate constant was the result. The respective ratios of the rate constants in 4.00 and 8.00 ml. solvent were the same within experimental error. Hence the poisoning effect explained above is not the only factor involved. This problem was not fully examined and afforded a possibility of further investigation into the exact equilibrium conditions.

The concentration of acceptor results were summarized in Table 7. In this table conditions other than pyridine concentration are standard.

The first irregularities in the rate curve were observed when the pyridine concentrations were increased. Oddly enough apparent breaks occurred in the vicinity of the calculated up-take of one and two equivalent moles of hydrogen. This is shown in Graph VI, and it led to the possibility of slow intermediate formation. The investigation of this was carried out by stopping a number of reactions at two-thirds completion and isolating the hydrogenated products and recovering the unreacted pyridine. The distillation was shown in Graph I, and no intermediate hydropyridines were found. Part (1) of the curve shows the isolated piperidine (52%), and part (2) represents the pyridine recovered (32%).

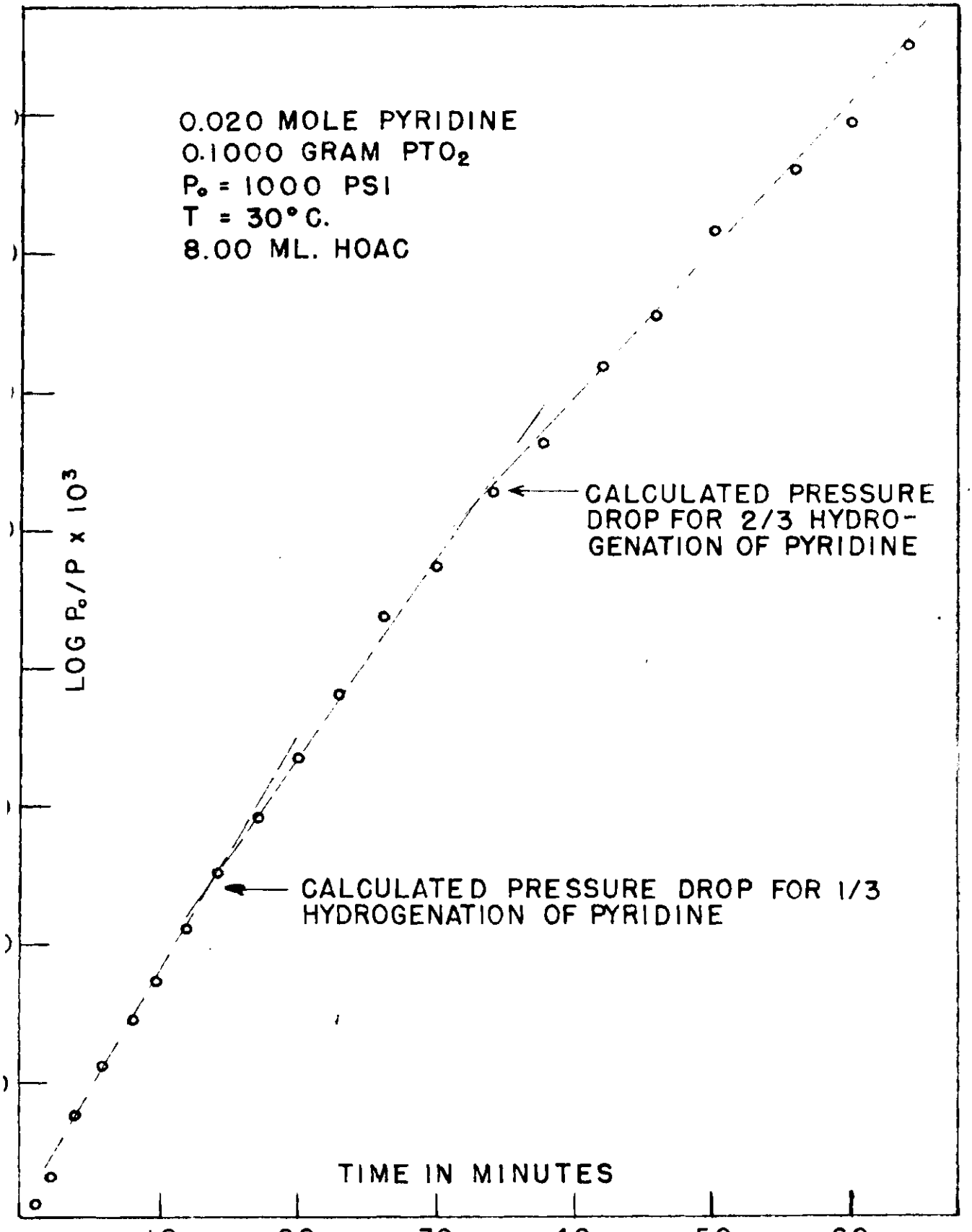
If the plot in Graph VI is viewed as being a gradual drift instead of having three different slopes, one could say that the reaction is not first order with respect to hydrogen pressure. This will be discussed in the next section.

Since the rate constant did vary with pyridine concentration, it seemed possible that the rate could be first order with respect to

Table 7. Effect of Concentration of Hydrogen Acceptor.

Compound	Moles Acceptor	Kv x 10^3 4 ml. HOAc	Kv x 10^3 8 ml. HOAc
Pyridine	0.010	423	684
	0.020	367	596
	0.040	343	524
2-methyl-	0.010	276	309
	0.020	256	-
	0.040	246	-
2,6-dimethyl-	0.010	178	-
	0.020	146	-
	0.040	141	-

GRAPH VI



EXAMPLE OF DRIFTING OF THE RATE CURVE FOR LARGE DROPS IN H_2 PRESSURE

pyridine. Thus equation (1) had to be modified so that the pyridine concentration at time t could be determined. The pyridine concentration, however, could be determined only in terms of the pressure drop of hydrogen. Thus equation (1) assumes a more complicated form:

$$\log \left(p + \frac{n_o \cdot 3RT}{v_g} - p_o\right) = \frac{-Kt}{2.303 v_1} + \log \frac{n_o \cdot 3RT}{v_g} \qquad (2)$$

where v_1= volume of solvent acceptor, v_g= volume of hydrogen, R is in cc-pounds per mole per degree, and n_o= moles acceptor used. A plot of

$$\log \left(p + \frac{3n_o RT}{v_g} - p_o\right)$$

against t should give a line of slope $-\frac{K}{2.303 v_1}$. Applying this relation to several sets of data, a straight line could be drawn over a larger pressure drop than before in some cases; but the gradual sloping off of the curve was still evident. The use of such an equation was not investigated further.

Effect of Initial Hydrogen Pressure

It was stated in previous sections that the reaction was probably not first order with respect to hydrogen pressure over large drops in pressure. Hence it was necessary to determine what the exact order might be.

As was previously shown, the equation:

$$\frac{p^{-n+1} - p_o^{-n+1}}{t(-n+1)} = K \qquad (3)$$

can be used for reactions in which different initial pressures are used, but the other conditions are the same. For this purpose initial pressures

of 500, 1000, and 1500 p.s.i. were selected. The final pressures were taken from the three runs at the theoretical absorption of two equivalent moles of hydrogen in order that the same amount of compound had been hydrogenated. The elapse of time for these pressure drops varied considerably. Substituting values for n (0.7, 0.8, 0.9), K values were calculated. Plotting the differences in K values for two separate pressure runs (500 and 1000, for example) against the assumed n gave a curve which crossed the x - axis at 0.95. The x - axis, of course, represented the value of n where there was no difference in K values. Therefore the order of the reaction with respect to hydrogen pressure is 0.95, since this value satisfies equation (3). Sample plots of this are shown in Graph VII.

In all runs in which 0.01 mole of acceptor was hydrogenated the pressure drop was between 100 and 300 p.s.i. Since the above calculations made between 500 p.s.i. drops showed the reaction to be close to first order, all Kv values have been calculated from the first order rate law. However, in the run (0.02 mole pyridine) plotted in Graph VI, the pressure drop was 600 p.s.i. Naturally, larger pressure drops were recorded for the hydrogenation of 0.04 mole of material. Thus we might conclude that the drifting of the curve in Graph VI is not entirely a poisoning, intermediate, or slow-rate effect, but it is probably due to the order being 0.95 with respect to pressure.

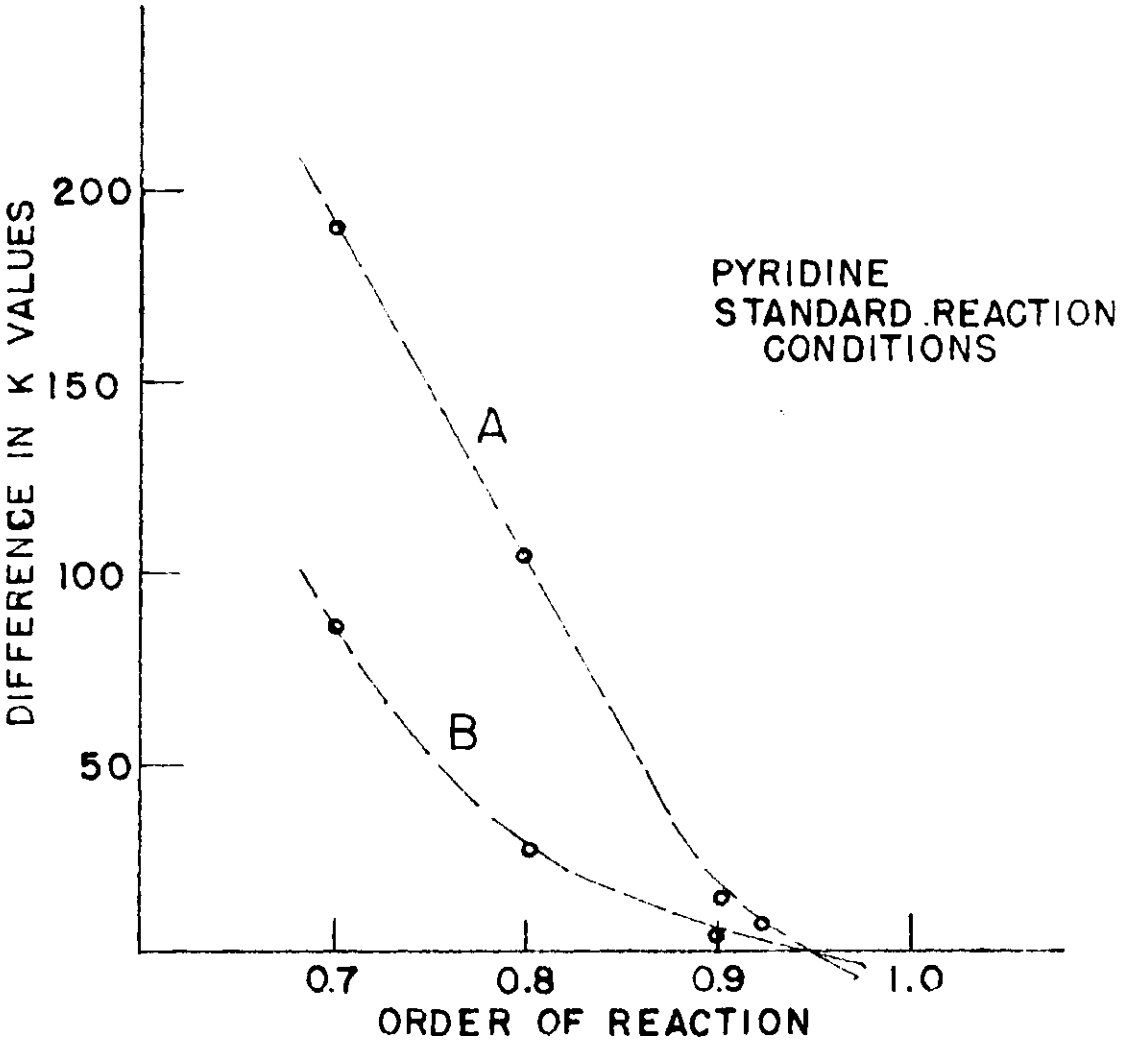
Table 8 shows the effect of varying the initial pressure.

Effect of the Amount of Catalyst

The rate of the reaction was found to be directly proportional to the amount of catalyst. In general, this was consistent with the

GRAPH VII

DETERMINATION OF THE ORDER OF THE REACTION WITH RESPECT TO HYDROGEN PRESSURE



(A) 500–1600 PSI
(B) 1000–1500 PSI

Table 8. Effect of Hydrogen Pressure

Compound	Initial Pressure	Kv x 10^3
Pyridine	500	471
	1000	423
	1500	369
4-methyl-pyridine	500	172
	1000	150
	1500	132
2,4-dimethyl-pyridine	500	175
	1000	144
	1500	130

kinetic studies of Smith and co-workers[26,27] and Stanfield[28] except in this investigation the maximum effectiveness of the catalyst was in the amounts 0.0100 to 0.1000 gram. In order to obtain this maximum effectiveness of catalyst, equilibrium conditions must be maintained at all times during the course of a reaction. It would seem that as long as the catalyst surface is covered by hydrogen acceptor that equilibrium conditions would exist. However, the problem is not as simple as this. For example, if there was too small an amount of solvent for the amount of catalyst, the rate would depend on the rate of solution of hydrogen. It was previously shown in this investigation that increasing the amount of solvent caused an increase in the rate constant. Also we have the possibility that there is a large concentration of acceptor for the amount of catalyst employed. This might lead to catalyst poisoning. On the other hand, if the amount of catalyst surface available is too large for the concentration of acceptor, equilibrium conditions can not be maintained. This was obviously the case when 0.1500 and 0.2000 gram of catalyst was used, and the exact equilibrium conditions were apparently being approached as the amounts of catalyst were decreased from 0.1000 to 0.0100 gram. In this latter range, a plot of Kv versus the amount of catalyst gave a straight line as shown in Graph VIII.

The catalyst runs are listed in Table 9, all under standard conditions. The third column relates the rate constant to a standard

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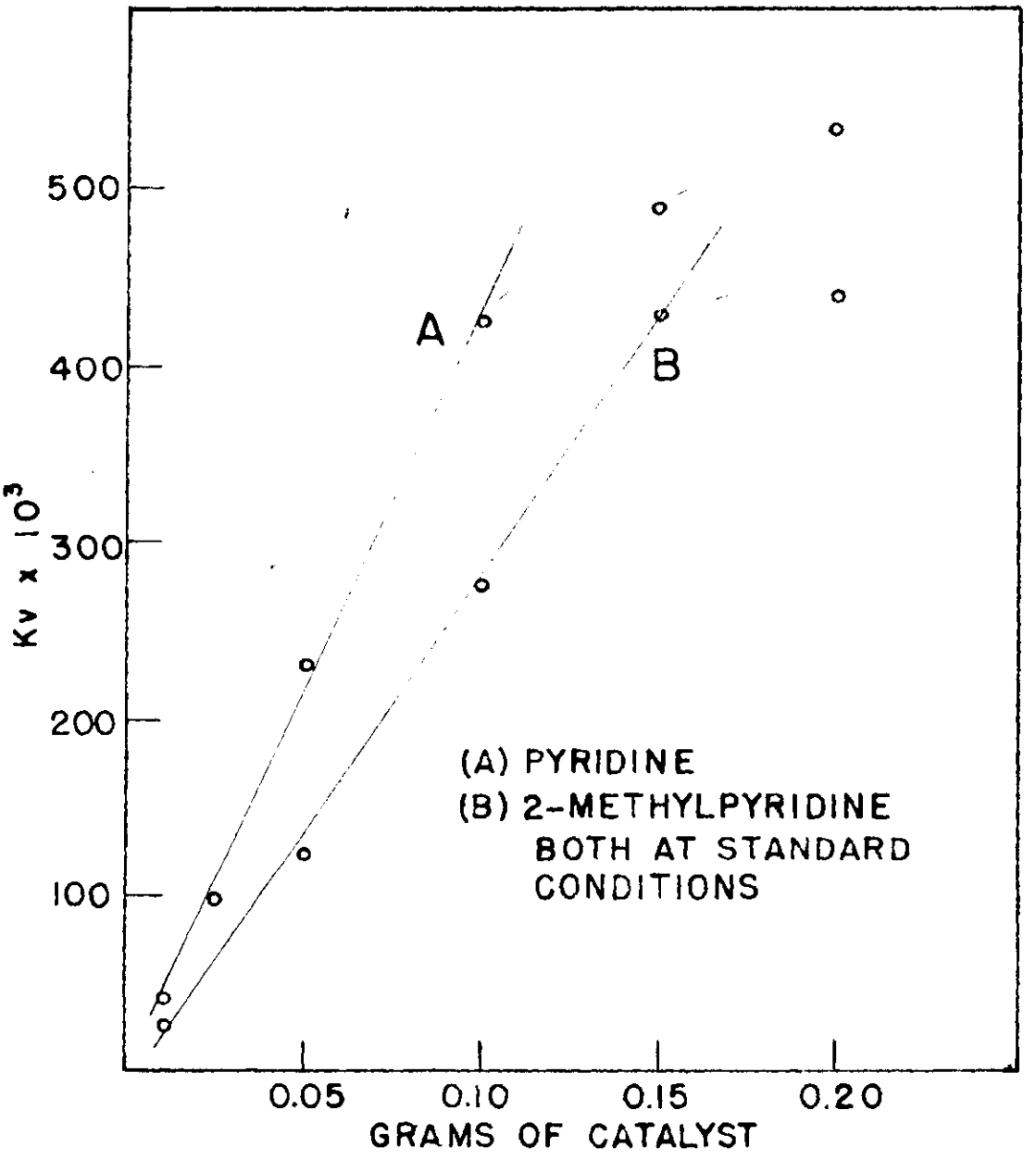
[26]Smith, H. A., Alderman, D. A., and Nadig, F. W., J. Am. Chem. Soc., 67, 272(1945).

[27]Smith, H. A., and Pennekamp, E. F. H., op. cit., p. 276.

[28]Stanfield, J. A., op. cit., p. 90.

GRAPH VIII



EFFECT OF THE AMOUNT OF CATALYST ON THE RATE CONSTANT

THE STRAIGHT PORTION OF THE PLOT SHOWS THE EFFECTIVE AMOUNT OF CATALYST RANGE.

Table 9. Variation in the Amount of Catalyst

Compound	Grams of Catalyst	Kv x 10^3	Kv x 10^3 per gram
Pyridine	0.0100	44.1	441
	0.0250	99.0	396
	0.0500	233	466
	0.1000	423	423
	0.1500	487	325
	0.2000	533	267
2-methyl-pyridine	0.0100	28.6	286
	0.0500	126	252
	0.1000	276	276
	0.1500	429	287
	0.2000	439	220
2,6-dimethyl-pyridine	0.0250	42.6	171
	0.0500	77.3	154
	0.1000	178	178
	0.1500	194	129

amount of catalyst, that is, one gram.

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